Epoxidation of α-pinene catalysed by tetrameric cobalt(III) complexes

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Abstract

A tetrameric cubane-like complex $[Co_4(\mu_3\text{-}O)_4(\mu\text{-}C_6H_5CO_2)_4(4\text{-}CNpy)_4]$ (**I**) has been prepared and characterised by various physicochemical techniques. Single crystal X-ray crystallographic studies on an analogous compound $[Co_4(\mu_3\text{-}O)_4(\mu\text{-}CH_3CO_2)_4(py)_4]$ (**II**) supports the presence of the $[Co^{III}_4(\mu_3\text{-}O)_4]$ cubane core in **I**. Complex **I** was examined as a catalyst for the homogeneous air oxidation of α-pinene under atmospheric pressure. Both temperature and catalyst concentration affect the reaction rate. High selectivity (62–68%) for α-pinene oxide formation is observed.
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Keywords: Co(III) catalyst; Cubane complex; Oxidation catalyst; α-Pinene epoxide; Selective epoxidation

1. Introduction

Oxyfunctionalization of cyclic olefins is of industrial importance due to the possibility of transforming cheap and readily available substrates to valuable intermediates for fine chemical synthesis. Terpenes, which are widely distributed in nature, are of particular importance from the fact that their oxidation products—terpenic aldehydes, alcohols and esters find use as the starting product for fragrance, flavour and therapeutic agent.

Several reports on autoxidation of monoterpenes including α-pinene, β-pinene and limonene in presence of cobalt(II) salts have appeared recently [1–6]. Most of these studies use environmentally unacceptable bromide ion promoters and/or acetic acid media resulting in complex mixtures of oxygenated derivatives with very low selectivities. Autoxidation of α-pinene with Co(OAc)₂/NaBr in presence of acetic acid gave verbenone, myretenal and *trans*-verbenyl acetate as the main products [2] in 10, 20 and 29% selectivity, respectively. Air oxidation of α-pinene with Co(II) pyridine complexes under solvent-free conditions led to allylic oxidation products, while air oxidation by cobalt(II) halide,

nitrate or acetate needed TBHP or glacial acetic acid as an activator [4,5]. Effect of solvent on the product distribution for the autoxidation of monoterpenes has also been reported [6]. In acetonitrile, a slow autoxidation occurs leading to equal amounts of epoxidation and allylic oxidation products, while products of substrate isomerization were observed in acetic acid. Similar retarding influence was also reported for benzene, chlorobenzene and dichloromethane [7].

Since the structure of monoterpenes has a considerable effect on the product distribution, ligand tuning as demonstrated for cobalt Schiff base catalysts [8,9] can play an important role in the outcome of the reaction. In this regard, oligonuclear oxo-bridged cluster complexes of transition metals may also provide a fundamental basis for the study of redox and ligand substitution reactions vital to metal catalysed autoxidation processes. Although trinuclear oxo-centred complexes of cobalt and manganese have been investigated [10,11] more thoroughly as oxidation catalysts, a couple of cubane-like complexes of manganese have also been found to catalyse the oxidation of a variety of organic substrates with TBHP as the oxidant [12]. These mixed-valent cluster complexes exhibit both oxygen atom transfer and hydrogen atom abstraction in catalytic oxidation reactions.

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In this paper we describe a process that uses a Co(III) based catalyst related to a reported heterogeneous catalyst effective for the autoxidation of alkylaromatics [13] for the oxidation of α-pinene to its oxygenated products. Novelty of our process lies in the fact that the metal species is already in the catalytically active +3 state and also because the complex contains a pyridine ligand. Since the Co(II) to Co(III) oxidation is a rate limiting step, presence of pyridine as a ligand accelerates the rate by stabilising the higher oxidation state of the metal.

2. Experimental

All materials used in this work were obtained from commercial sources and used without purification. $Co(NO_3)_2 \cdot 6H_2O$ and hydrogen peroxide were purchased from E. Merck (India). Both 4-cyanopyridine and α-pinene were purchased from Aldrich Chemical Company (USA). Sodium salt of benzoic acid (SRL, India) was prepared by neutralising the acid with sodium hydroxide and the salt obtained by evaporation was further purified by recrystallization. Methanol used was of reagent grade. Infrared spectra in the mid-IR region (4000–450 cm^{-1}) were recorded using a Perkin Elmer RX1 FT-IR spectrophotometer for KBr pellets. UV–vis spectra were recorded on a Perkin Elmer Lambda 40 spectrophotometer. Electrochemical studies were performed under N_2 environment on a BAS 100B Electrochemical Analyser using a three-electrode cell assembly. A glassy carbon disc was used as working electrode with Ag–AgCl as the reference electrode. ^{1}H NMR spectrum was recorded on a JEOL 270 MHz instrument. GC data were obtained on a Varian 3800 gas chromatograph, while for GC-MS data a Finnigan MAT Magnum instrument was used.

2.1. Preparation of $[Co_4(\mu_3\text{-}O)_4(\mu\text{-}O_2CC_6H_5)_4(4\text{-}CNpy)_4]\cdot 2CH_2Cl_2(\textbf{I})$

$Co(NO_3)_2 \cdot 6H_2O$ (2.90 g, 10 mM) and sodium benzoate (2.88 g, 20 mM) are stirred in methanol (45 mL) and heated to refluxing temperature and 4-cyanopyridine (1.04 g, 10 mM) is added to the stirred reaction mixture. The 30% hydrogen peroxide (v/v, 6 mL, ~60 mM) is slowly added to the reaction mixture and stirring under refluxing condition is continued for 4 h. The olive green compound precipitating out is filtered from the cooled reaction mixture. The compound is then recrystallized from a mixture of dichloromethane and petroleum ether (60–80 fraction). It is dried in a vacuum desiccator over fused calcium chloride. Yield: 2.07 g (70%). Anal. calcd. for $C_{54}H_{40}N_8O_{12}Cl_4Co_4$: C, 46.39; H, 3.01; N, 7.45%. Found: C, 47.29; H, 2.92; N, 8.17%. ^{1}H NMR (270 MHz; DMSO-D$_6$): δ 9.06(d, 8 H), δ 8.13–8.17(m, 16 H), δ 7.68–7.84(m, 12 H) [d, doublet; m, multiplet]. UV–vis spectral data: (CH$_2$Cl$_2$) λ_{max}: 629 nm (ε = 511 $M^{-1}cm^{-1}$), 446 nm (sh), 351 nm (sh). IR spectral data (KBr): ν_{max} (cm^{-1}) 3020(w), 2900(w), 2239(m), 1610(m), 1590(m), 1523(s), 1490(s), 1383(vs), 1220(m), 1176(m), 1066(w), 1026(m), 833(m), 794(w), 765(w), 722(s), 695(m), 637(m), 593(m) and 579(m) [vs, very strong; s, strong; m, medium; w, weak].
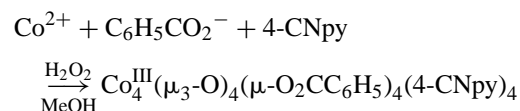
2.2. Air oxidation of α-pinene

A typical air oxidation of α-pinene was carried out in a round-bottomed flask equipped with a reflux condenser, a gas inlet and a magnetic pellet. A definite amount of catalyst **I** was suspended in the reaction mixture consisting of α-pinene in 40 mL of 1,4-dioxane. Air (15 mL/min) was bubbled through the stirred reaction mixture. Samples of the reaction mixture were withdrawn at different time intervals for GC analysis. Air oxidation products were identified by GC-MS and also by comparing them with authentic samples.

3. Results and discussion

3.1. Synthesis and characterization of $[Co_4(\mu_3\text{-}O)_4(\mu\text{-}O_2CC_6H_5)_4(4\text{-}CNpy)_4]$ (**I**)

The tetrameric cobalt(III) complex was prepared by oxidising cobalt(II) ions in the presence of the N-donor ligand 4-cyanopyridine and benzoate ions

$$Co^{2+} + C_6H_5CO_2^- + 4\text{-CNpy}$$
$$\xrightarrow[\text{MeOH}]{\text{H}_2\text{O}_2} Co_4^{III}(\mu_3\text{-O})_4(\mu\text{-O}_2CC_6H_5)_4(4\text{-CNpy})_4$$

This compound may also be prepared at 30 °C without sacrificing either yield or purity. The substituted pyridine ligand stabilises the +3 oxidation state of cobalt to facilitate the formation of complex **I**. Recrystallization of the compound from a dichloromethane/petroleum ether mixture leads to a solvated product containing two molecules of CH$_2$Cl$_2$. The isolated crystals lose crystallinity with time, probably due to the loss of solvent. This prevented us from analysing the crystals with single crystal X-ray diffraction. The olive green product was characterised by vibrational, electronic, ^{1}H NMR spectroscopy and cyclic voltammetry.

The Co(III) complex (**I**) is substitutionally inert; the structure of the complex is retained for a long time after it is dissolved in a solvent. The diamagnetic nature of complex **I** is evident from its ^{1}H NMR spectrum where the aromatic protons belonging to the benzoato and 4-cyanopyridine ligands appear at expected positions. The complex has also been studied by infrared and UV–vis spectroscopy. In its IR spectrum, it is possible to identify bands due to the bridging benzoate anions as well as for the pyridyl-N bound 4-cyanopyridine ligands. The separation of the asymmetric and symmetric stretching vibrations ($\nu_{asym} - \nu_{sym} = \Delta\nu = 139\,cm^{-1}$) of the carboxyl group is consistent with this ligand bonding in a bridging fashion. A weak but sharp band at 2239 cm^{-1} indicates the presence of 4-cyanopyridine ligand.
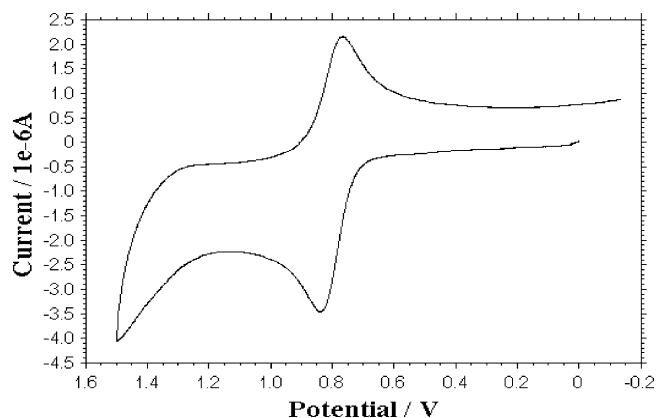
Fig. 1. Cyclic voltammogram for a CH_2Cl_2 solution of compound **I** at a scan rate of $100\,mV\,s^{-1}$ with tetrabutylammonium perchlorate as the supporting electrolyte.

Three visible spectral bands were observed for the complex **I**, the band at 629 nm and the shoulder at 446 nm are attributable to spin-allowed d–d transitions $^1A_{1g} \rightarrow\ ^1T_{1g}$ and $^1A_{1g} \rightarrow\ ^1T_{2g}$ respectively for low-spin Co(III) complexes [14], while the band at 351 nm is characteristic of a ligand to metal charge transfer transition involving the μ_3-O-Co(III) moiety present in complex **I**. The corresponding absorptions for complex **II** also appear at similar positions.

The cyclic voltammogram obtained for a CH_2Cl_2 solution of **I** shows (Fig. 1) a nearly reversible reduction with $E_{1/2}$ = 0.80 versus Ag/AgCl. It is imperative that the tetrameric $[Co^{III}Co^{III}Co^{III}Co^{III}(\mu_3$-O$)_4]$ core undergoes a one-electron reduction to form a species containing the reduced $[Co^{III}Co^{III}Co^{III}Co^{II}(\mu_3$-O$)_4]$ core, which is also stable. However, a recent report by Christou and co-workers [15]

on the complex $[Co_4(\mu_3$-O$)_4(\mu$-O$_2CCH_3)_2(2,2'$-bipy$)_2]^{2+}$, which is structurally related to complex **II**, $[Co_4(\mu_3$-O$)_4(\mu$-O$_2CCH_3)_4(py)_4]$ (please see below), indicates that their complex containing a cubane-like 'Co$_4(\mu_3$-O$)_4$' core is oxidised to $[Co^{III}Co^{III}Co^{III}Co^{IV}(\mu_3$-O$)_4]$. This is contrary to the popular belief that in cobalt-catalysed oxidations the oxidation states of cobalt cycle between +2 and +3. Nevertheless, such favourable electrochemical reduction potentials for complexes **I** and **II** ($E_{1/2}$ = 0.89 V versus Ag/AgCl) make these compounds interesting candidates for use as catalysts for the oxidation of organic substrates. More importantly, because the reduced and oxidised species can go from one state to the other reversibly it may be possible to use the catalyst repeatedly for redox catalysis.

The analogous cubane-like cluster complex $[Co_4(\mu_3$-O$)_4(\mu$-O$_2CCH_3)_4(py)_4]$ (**II**) prepared by us was characterised by single crystal X-ray diffraction. Single crystal X-ray diffraction measurements on **II** were made with a Bruker SMART-CCD diffractometer employing graphite monochromatised Mo Kα radiation (λ = 0.7107 Å). Crystallographic data are: triclinic, P$\bar{1}$ = 10.196(2) Å, b = 11.262(3) Å, c = 34.539(8) Å, α = 87.55(5)°, β = 89.75(4)°, γ = 76.91(4)°, V = 3859 Å^3, z = 4, R1 = 0.2260 for 13,101 $[F_0 > 4\sigma(F_0)]$ reflections and 0.2446 for all 16560 data. The high residuals obtained for the structure are likely to be due to poor quality of the crystal (intensity data) used. However, apart from non-hydrogen atoms included in the molecular structure, there were no significant electron density peaks chemically assignable to any other atoms. This proves the essential correctness of the molecular structure. A molecular structural diagram of complex **II** is shown in Fig. 2. The asymmetric unit of the crystal structure consists of two isolated molecules of
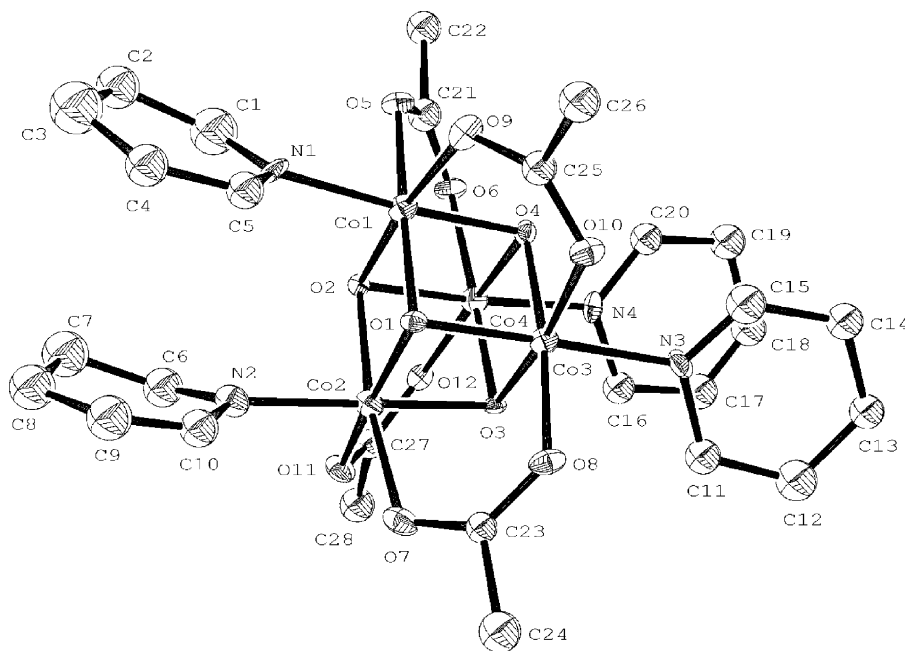

Fig. 2. An ORTEP diagram of $[Co_4(\mu_3$-O$)_4(\mu$-O$_2CCH_3)_4(NC_5H_5)_4]$ (**II**).
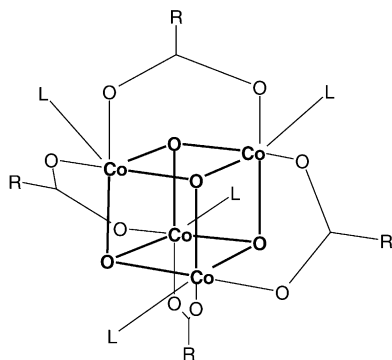
Fig. 3. Proposed structure of complex **II**, where L = 4-CNpy and R = C_6H_5.

II, although we have presented only one tetrameric molecule in the figure. Geometrical parameters for both molecules, within experimental errors, are comparable. Four each of Co^{III} and O^{2-} ions present in the alternate corners of the cube form an approximate cube-like core in this complex. The oxide anions thus act as μ_3-bridging ligands. The structure has four cobalt atoms and four oxygen atoms (O^{2-} ions) occupying the corners of an approximate cube. Pyridine ligands occupy the most outlying sites on the octahedral Co(III) centres. All four cobalt atoms are thus in the +3 oxidation state and as expected for d^6-Co^{3+} ions, the metal centres adopt low-spin diamagnetic configurations under the octahedral ligand environment. The average Co—O and Co—N distances are 1.87 and 1.93 Å; two types Co···Co distances close to 2.70 and 2.81 Å are also observed as in the previously determined structures of cobalt(III) complexes having a 'Co$_4$(μ_3-O)$_4$' core of a substantially distorted cubic geometry [16,17]. We believe that complex **I**, prepared under similar conditions with complex **II**, showing similar physicochemical characteristics with the latter also has an analogous molecular structure (Fig. 3) with four 4-cyanopyridine ligands replacing the sites occupied by pyridine ligands in **II**. In view of the fact that the nitrile vibration in the 4-cyanopyridine ligand occurs at 2239 cm^{-1}, which is close to that of uncoordinated 4-cyanopyridine (2243 cm^{-1}), the coordination has most likely occurred through the pyridyl end as observed in **II**.

3.2. Catalysed air oxidation of α-pinene

Catalytic oxidation of olefins proceeds through two important pathways: epoxidation and allylic oxidation. Epoxidation involves an electrophilic attack on the double bond while allylic oxidation results from allylic H-abstraction. Both re-

actions involve free radical intermediates and are competing processes. Occurrence of either the former or the latter mechanism is not only related to the nature and oxidation state of the metallic species, but it also depends on the nature of the olefin used as well as the relative stability of the radicals formed.

Verbenone, an allylic oxidation product of α-pinene, is used as a building block of taxol [18] and thus we decided to explore the oxidation of α-pinene catalysed by complex **I**, which is more soluble than complex **II** in organic solvents. As will be seen from the results described below, the reaction has led to both epoxidation and allylic oxidation products (Scheme 1), with preference for the former.
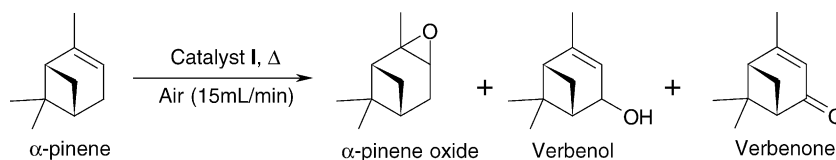
3.2.1. Effect of reaction temperature

The effect of reaction temperature was studied by adding a known amount of catalyst (**I**) (25 mg, 0.08 mol%) to the reaction mixture of α-pinene (3.97 mL, 25 mmol) in 40 mL of 1,4-dioxane and by passing air (15 mL/min) through it. The reaction mixture was then heated to 60, 80 or 100 °C, respectively, and the progress of the reaction was monitored by GC. Results are shown in Table 1. Our results show that an increase in the reaction temperature accelerates air oxidation of α-pinene with the highest conversion of 66.8% being observed at 100 °C after 24 h. In all the three temperatures air oxidation commenced quickly with a preferential formation of α-pinene oxide over other oxidation products.

3.2.2. Effect of catalyst concentration

To optimize the catalyst requirement in the air oxidation of α-pinene, the catalyst concentration was varied between 0.01 and 0.5 mol%. To a reaction mixture of α-pinene (3.97 mL, 25 mmol) in 40 mL of 1,4-dioxane an appropriate amount of catalyst was added and then air (15 mL/min) was bubbled through it. Periodically, samples were taken out and analysed by GC. The results have been plotted in Fig. 4. The highest substrate conversion in the reactions is 81.4% with a turnover frequency (TOF) of 105 after 24 h, while the selectivities for the epoxidation product, α-pinene oxide, are in he range of 62–68%. It can be seen that conversion and product yields are the highest when catalyst concentration is the lowest. This is in conformity with an earlier report where higher concentration of catalyst led to slower air oxidation of α-pinene [4].

In all our experiments, oxidation of α-pinene yielded α-pinene oxide as the main product, together with verbenol and verbenone as the other products. Rearrangement of α-pinene oxide also produced a minor amount of α-campholene

Scheme 1.

Table 1
Effect of reaction temperature on α-pinene oxidation by complex **I** under atmospheric pressure[a]

Reaction temperature (°C)	Conversion (%)	Composition of product mixture (%)			
		α-Pinene oxide	Verbenol	Verbenone	Other products
60	6.97	3.5	1.28	2.19	0
80	30.62	9.73	5.07	7.9	7.92
100	66.84	31.43	4.76	15.19	15.46

[a] Conditions—α-pinene: 3.97 mL (25 mmol); catalyst: 25 mg (0.08 mmol); 1,4-dioxane: 40 mL; oxidant: air (15 mL/min); reaction time = 24 h.

aldehyde, a ring contracted aldehyde, typical of monoterpene oxides under the influence of a Lewis acid. In all cases maximum yield of epoxide was observed after 24 h; prolonging the reaction to 46 h led to the steady decrease in the amount

Fig. 4. Effect of catalyst concentration (0.01, 0.08 and 0.5 mol%) on air oxidation of α-pinene after 24 h.

of α-pinene oxide indicating that the rate of rearrangement of epoxide had taken precedence over epoxidation. Steady increase in the amount of verbenone beyond 24 h is significant from the fact that, at that stage the allylic oxidation pathway becomes more pronounced than the epoxidation pathway.

In contrast to our results described above, Lajunen and Koskinen [19] found verbenone, the allylic oxidation product, to predominate both in solvent-free and liquid phase reactions catalysed by Co(II) complexes. Our results indicate a marked preference for the epoxidised product in all cases. The maximum conversion observed was over 81% with epoxide yield of over 48% at the end of 24 h with 0.01 mol% of catalyst. Epoxide yield and selectivity observed with our catalyst are much higher compared to other reports where either a co-oxidant or a promoter is used along with a Co(II) catalyst [5]. Product selectivity for α-pinene oxide is better with our catalyst compared even to the rare instance [7] where the epoxidation reaction takes precedence over allylic oxidation in α-pinene autoxidation processes catalysed by a variety of catalysts.

In absence of solvent only a small amount of α-pinene oxide is detected in the reaction mixture after 24 h, which is likely to be due to the skeletal rearrangement of epoxide under the conditions used. This view is supported by the fact that air oxidation of α-pinene oxide itself under similar reaction conditions results in the formation of the rearranged products, viz. α-campholene aldehyde and *trans*-pinocarveol along with other minor products. In acetonitrile the reaction rate and product selectivities decrease significantly resulting in approximately equal amounts of epoxidation and allylic oxidation products. However, it is worth pointing out that unlike in the instance where an induction period of 3 h is observed in acetonitrile at 100 °C [4], we observed no induction period prior to product formation. A conversion of 11% was observed after 3 h. Use of 1,4-dioxane permits us to avoid the concomitant rearrangement to attain 62–68% selectivity for α-pinene oxide, which can be considered significantly high for reactions involving free radicals. Good solubility and stability of complex **I** in 1,4-dioxane also provides an added advantage to use it as the solvent for the homogeneously catalysed reactions.

Our studies also indicate that the nature of the metal complex used as the catalyst for the oxidation of α-pinene does not change too much at the end of the reaction. The isolated used catalyst is also olive green in colour and it shows similar UV–vis absorption characteristics with complex **I** (Fig. 5). This indicates the stability of the catalyst under autoxidation
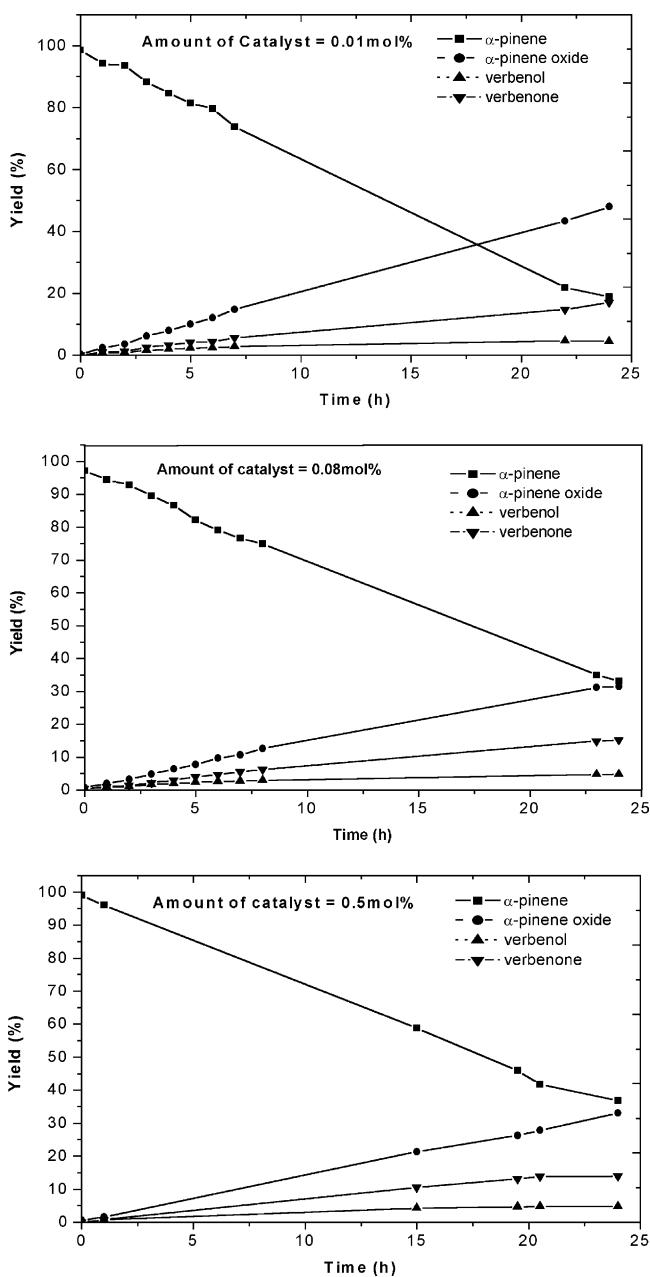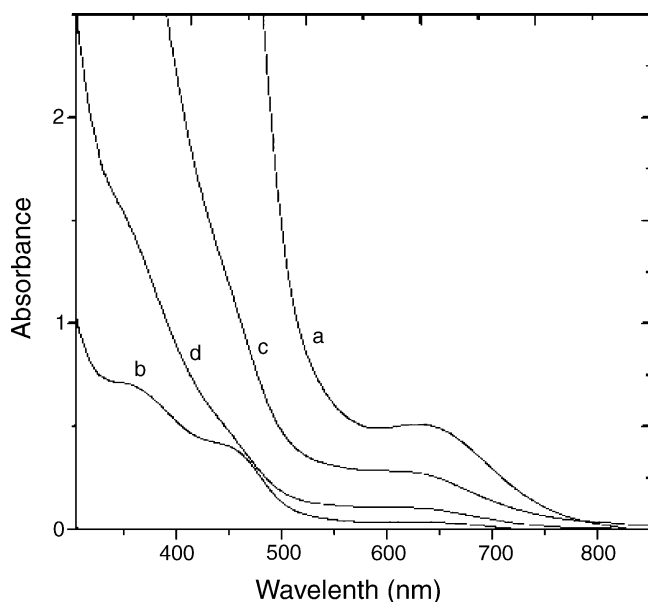
Fig. 5. UV–vis spectra recorded in CH_2Cl_2: (a) complex **I** (10^{-3} M), (b) complex **I** (10^{-4} M), (c, d) used catalyst at different concentrations.

conditions. This view is also corroborated by infrared spectral results.

4. Conclusion

An efficient homogeneous catalyst system for the selective formation of α-pinene oxide through air oxidation of α-pinene has been developed. Unlike any of the previous reports on α-pinene autoxidation, we have used a cobalt catalyst containing the metal in the +3 oxidation state and as a result, induction period was not observed. The rate of reaction is dependent on temperature and catalyst concentration. A catalyst concentration of 0.08 mmol, a reaction temperature of 100 °C and a reaction time of 24 h have been found to be optimum for high conversion of α-pinene and high selectivity to α-pinene oxide yield.

Acknowledgements

Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molcata. 2004.02.028.

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